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SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
NRL Memorandum Report 4845 A D 2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitie)	S. TYPE OF REPORT & PERIOD COVERED
MERCURY CONTAMINATION OF A COMMUNITY WATER SUPPLY — DIAGNOSIS AND RESTORATION	Final report.
WATER SUITE I - DIAGNOSIS AND RESTORATION	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(*) J.C. Cooper, C.J. Hackbarth, C.M. Hellwig, Rm. Panayappan, and D.L. Venezky	8. CONTRACT OR GRANT NUMBER(*)
9. Performing organization name and address Naval Research Laboratory Washington, DC 20375	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS	July 7, 1982 13. NUMBER OF PAGES 42
14. MONITORING AGENCY NAME & ADDRESS(II dillerent from Controlling Office)	15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)	<u> </u>

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Mercury Contamination Water supply Chemical cleaning

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A community water supply was contaminated by mercury from a flow meter. The subsequent chemical analyses, sampling methods and chemical cleaning methods employed for diagnosing and resolving the problem are described. The results show (1) that significant errors in evaluating such a problem could result from inadequate or incorrect sampling methods or sampling site selection, (2) that complications in the interpretation of the results arise from the chemistry of the water system and the surfaces of the plumbing system, and (3) that small portions of the water system are likely to be major sources of contamination and can be cleaned efficiently by chemical means. Recommendations are made concerning the use of mercury-containing flow meters.

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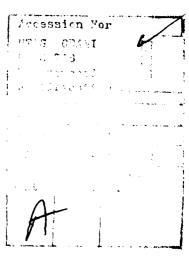
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MERCURY CONTAMINATION OF A COMMUNITY WATER SUPPLY DIAGNOSIS AND RESTORATION

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INTRODUCTION

This report describes the occurrence of a mercury spill, discovered in early March of 1978, from a mercury-filled flow meter into a community water supply and the subsequent evaluation and correction of the problem. Difficulties encountered with sampling methods and with standard methods for analysis of mercury could complicate the diagnosis and resolution of similar problems in other drinking water supplies. Such other occurrences are likely since mercury-containing flow meters are in common use. The information presented here should help to prevent such incidents and if they do occur, significantly aid in their resolution.

The water supply studied consists of two operating wells, each approximately 500 feet deep, in different aquifers pumping on demand into either the distribution system with a volume of about 150,000 gallons or a 100-foot-high reservoir tower with a capacity of about 500,000 gallons. The system supplies water to about 25 residences in addition to laboratory buildings, involving a total of about 250 people. Figure 1 shows the general layout of the distribution system. The majority of the main distribution lines are 14-inch and smaller transite pipe. Some areas, such as the distribution valves and plumbing near the water tower are cast iron and provided a significant complication in the spread of mercury into the distribution system.

Figure 2 shows the relationship of the well pumphouse where the mercury entered the system to the water tower and distribution valve area. The 8-inch well is a total of 540 feet deep through alternating shale and sandy loam aquifers. A submersible pump and a check valve are located at the bottom of a 240 foot inner sleeve of 4-inch black iron. The actual water level is approximately 100 feet above the pump under normal conditions. A mercury flow meter of a Ledoux Bell design (Figure 3) measures water flow by calculation of the pressure differential on either side of a standard orifice. The combined effect of a faulty check valve above the pump, the location of the

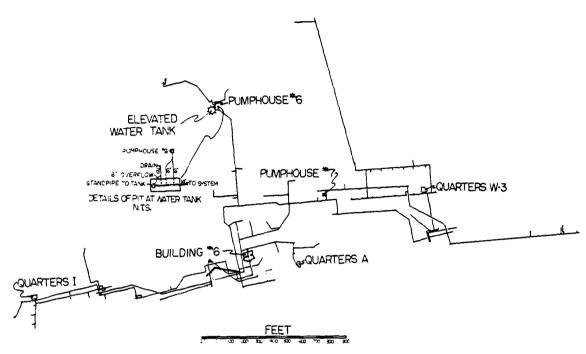


Fig. 1 - Drinking water distribution system major features, CBD/NRL. Routine sampling locations indicated.

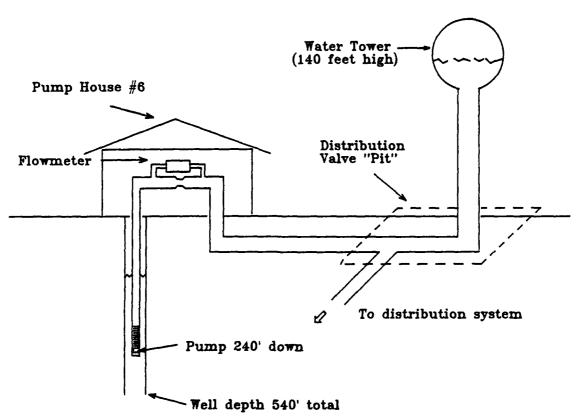


Fig. 2 - Schematic of well system. (not to scale).

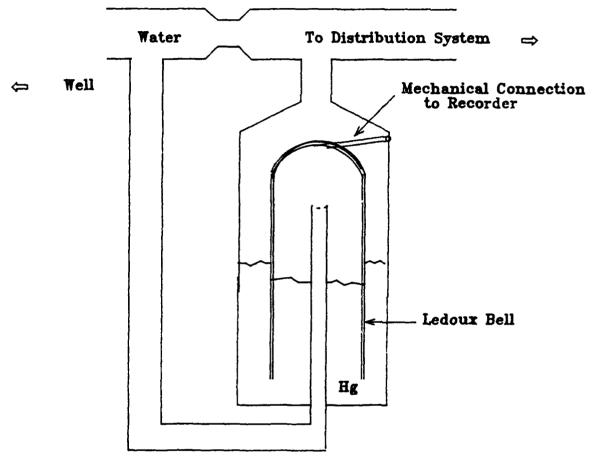


Fig. 3 - Approximate design of mercury flow-meter which delivered mercury into water system.

mercury flow meter with respect to a second functional check valve and the limited tolerable pressure differential of the flow meter was to siphon mercury from the flow meter into the line leading from the well. Immediate action was taken to prevent further contamination, diagnose the problem, and restore the system to safe concentrations of mercury. The sequence of events to accomplish these goals are reported here, and the appendix tabulates, chronologically, mean values of malyses performed through October, 1978.

EXPERIMENTAL PROCEDURES

Samples were collected in new, conventional polyethylene bottles which had been pretreated by soaking with 50% nitric acid for at least 24 hours, followed by a thorough rinsing with pure water (Milli-Q-process, producing water of higher overall quality than ASTM Type III: ASTM-D1193-77). During the first phases of sampling, a blank containing Millipore water traveled with the sample bottles throughout and always measured below our detection limit of 0.18 μ g/l (ppb). Some bottles containing samples measuring less than 7 μ g/l in total mercury were recycled by soaking with nitric acid as above.

Initial experiments showed no detectable leaching of mercury from such recycled bottles even after standing several weeks. Subsequently however, it was found that solutions containing a known amount of additional mercury typically showed analytical results lower than expected, presumably due to surface scavenging of mercury by residual materials (probably iron oxides) not completely removed by the cleaning process, or by otherwise activated surface materials. Although a substantial fraction of samples were collected in recycled bottles, the slight amount of mercury loss combined with timely analyses ensured that this phenomenon did not in any way affect any of the conclusions.

If more than 48 hours were to pass between time of sampling and analysis, samples were acidified with nitric acid to pH=2.0. As a result, no differentiation between oxidation state of mercury in the samples could be made in those cases. With the exception of re-runs of older samples and similar studies of day-to-day repeatability and sample aging experiments, in excess of 95% of the samples were analyzed within 48 hours of sampling, and none were held more than 96 hours before analysis.

To avoid the inconveniences which a random sampling method would impose upon residential users, a plan for continuous monitoring of selected locations was devised, coupled with occasional sampling of all residences. Occasional additional sampling points were added at random as a check on the statistical validity of the selected loca-

tions. Three residences were chosen so as to allow sampling of three main portions of the distribution system (Fig. 1). In addition, regular sampling was done at Building 6 (a location used for some specific tests of sampling methods), pump house 6 (the contaminated well), and pump house 7 (to insure the integrity of the water supply in use and to check for possible geological migration from well no. 6). Sampling at these locations was done on a weekly schedule with additional sampling during periods of system perturbation.

Analysis Methods. With the exception of some x-ray fluorescence analyses² done to verify results and to aid in differentiation of oxidation state, all mercury analyses were performed using the standard EPA method of manual cold-vapor atomic absorption.³ Initial analyses showed no organic mercury compounds present. The mercury analysis equipment is shown in Figure 4. Analyses were performed on one of two instruments - a Perkin-Elmer 460 double-beam or P.E. 272 single-beam atomic absorption spectrometer. In both cases, a mercury hollow-cathode lamp was used and the measurment was made at the 253.7 nm line of mercury. With the exception of a difference in absorbance vs. concentration slopes for the two instruments, error-of-measurement data showed no significant differences between the two instruments, provided the single-beam instrument was re-zeroed frequently enough to correct for its continuous drifting.

Unless otherwise stated, mercury analytical results are for total mercury. The sample was homogenized by vigorous shaking before removing an aliquot and the reported results are for three or more runs with standard deviation less than 10% of the value reported. Samples showing greater than 11 μ g/l for a 100 ml aliquot were diluted and rerun. Mercury in solids such as scale was determined by digesting weighed samples in boiling aqua regia for at least four hours and diluting with water. Standard addition experiments established a lower detection limit of 0.18 μ g/l using water samples from the water system. Operator-to-operator variations and volumetric errors were found to be insignificant. The only significant contributions to measurement error were due to the sampling itself.

Analyses for iron and copper in the various cleaning operations were done by standard flame atomic-absorption methods.³

Auger measurements⁵ on scale inside the cast-iron plumbing in the valve-pit area involved standard methods. However, considerable vacuum drying was required, possibly causing some loss of elemental mercury.

Reagents were all of ACS Reagent Grade or higher purity. The chemicals for the cold vapor mercury analyses were specially prepared

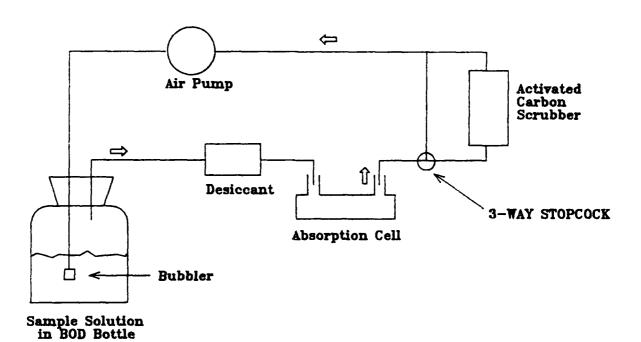


Fig. 4 - Cold - vapor mercury analysis system.

to be low in mercury. Standards were freshly prepared each day from 0.001 to 0.1 M stock solutions by serial dilution. In the case of the mercury standards, two stock solutions from entirely unrelated sources were prepared by different operators. Analyses by both AA and by x-ray fluorescence gave results in agreement within experimental error in both cases.

ANALYSIS AND RESOLUTION

The first evidence that a problem existed was the indication from flow meter service personnel that several pounds (between 7 and 14.5 lbs) of mercury had been replaced. Subsequent analysis of a single sample from a residential location (Quarters A in Fig. 1) showed a total mercury concentration of 97 $\mu g/1$, a level some fifty-fold higher than the established maximum permissible level for public drinking water supplies of 2 $\mu g/1^6$ and some 2000 to 5000 times the likely background levels. 7 , 8

Immediate action was taken to prevent further contamination. well and associated plumbing were isolated from the distribution system. The offending flow meter and one at a second well site (pump house no. 7 in Fig. 1) were irreversibly removed from the system. Physical removal of contaminated water and any localized pools of mercury was initiated by flushing the entire distribution system with water from the reservoir tower. At this point, efforts were begun to determine (1) the extent of the spread of elemental mercury into the system, (2) the true system level of mercury, and (3) the location of the bulk of the mercury. At the same time, studies were undertaken to validate our sampling methods. In addition, because the mercury concentration was at the body-burden level and because the duration of the problem was uncertain, personnel using the water system were screened (single-void urine samples) for mercurypoisoning. Results indicated essentially normal levels of mercury (about 5 μ g/1) in urine of all residents, suggesting the contamination was recent. In addition analyses of ice cubes, an emergency water supply, and water from a closed-off portion of the distribution system showed the problem to be less than 6 months, but more than two weeks old.

Localization of Mercury. The water system itself provided complications which would likely spread mercury throughout the distribution system and which made distribution of the mercury difficult to determine. First, there are at least three possible oxidizing agents or catalysts for the ready conversion of elemental mercury to soluble mercury(II) which would readily spread: dissolved oxygen, chlorine from the chlorination systems located in each pump house at the outlet of the well, and iron(III) present in scale in the plumbing. Second,

the system operates so that water is pumped by either pump into the reservoir or into the distribution system as needed, thus making impossible any prediction of the direction elemental mercury droplets might be conveyed. Third, sampling points were not readily available in the general vicinity of the flow meter.

After an initial determination by selected sampling that mercury at levels above 20 μ g/l was to be found in each major section of the system, a program was begun of physically flushing the distribution system with water from the reservoir (up to 1/2 million gallons each time at once-or twice-weekly intervals). A comprehensive sampling was done of all residences and such other sampling points as were accessible to provide enough data to allow statistically valid conclusions about levels of mercury in various parts of the system.

Initial results after several physical flushing operations indicated the following: (1) levels of total mercury were generally about the same, ranging from 6 to 20 µg/1 at the cold water taps indicating thorough distribution, (2) the lower elevation locations (near Quarters I in Fig. 1) were generally at the high end of this range, (3) the uncontaminated well was usually at or below our estimated detection limit of 0.18 µg/l mercury, indicating no appreciable geological migration from the possibly contaminted well to the lower aquifier of well no. 7, (4) mercury levels at a sampling tap near the chlorination equipment of pump house no. 6 were often in excess of 200 µg/1 with visible mercury droplets sometimes observed, (5) sampling from the bowl of the reservoir tower showed levels similar to the rest of the system, but the mercury was nearly all in the suspended solids (5 to 8 μ g/l total Hg) and not in solution (0.3 μg/1 soluble Hg), (6) samples taken from drain taps of hot water heaters in residences were sometimes very high in total mercury (several greater than 100 μ g/1, highest was 1500 μ g/1) and subsequent analyses showed the mercury in these samples to be nearly all in the suspended solids (soluble mercury was less than the total mercury level of the corresponding cold water sample).

At this point, it was apparent that the physical flushing of the distribution system had reduced somewhat the overall levels of mercury in spite of concern that this might further distribute any local concentrations of elemental mercury. It was also apparent that mercury existed in the system as soluble mercury(II), elemental mercury, and possibly as a mercury(I) compound in the suspended solids. In addition, much higher mercury concentrations in samples near pump house 6 and very high concentrations in samples from a tap in the pump house indicted the bulk of the mercury was still in the vicinity of pump house 6.

Inasmuch as high levels of mercury were found in the vicinity of pump house 6, two portions of the system were opened for sampling. The plumbing at the point of attachment of the flow meter contained approximately 1.5 lbs. of elemental mercury, mostly in the dead space of 'TEE's' and valves. The entire section of lines in the pump house, up to the well head, was dismantled and physically cleaned. In addition, the distribution valve area, the next accessible portion of the system near pump house 6 and common to the water tower and the distribution system (see inset in Figure 1), was entered by removing a section of pipe outside the pit area and two valve stems in the pit. Although there were no large pools of elemental mercury, some mercury droplets were found and the soluble mercury levels were considerably higher (about 70 μ g/1) than at the end points of the distribution system. In addition, scrapings of the scale from inside plumbing in the pit area had high mercury levels (0.05% by weight). Tests using uncontaminated water standing in the section of pipe that was removed gave 20 µg/1 levels of total mercury in the water after standing one hour. A significant portion of the soluble mercury in the distribution system could be leaching from the iron-oxide scale. It was determined that some sort of cleaning of this portion of the system would be required. In addition, since these operations had not accounted for the bulk of the approximately 14 lbs. of mercury thought to have entered the system, it was likely in the well. Very high levels (sometimes greater than 1000 µg/1 and containing droplets of mercury) in water pumped from well no. 6 into a collecting tank confirmed this latter point. It would therefore be necessary to clean the well.

Cleaning Operations. The cost of a new well and the risk of further environmental damage from a contaminated abandoned well required a method of removal of mercury from the well or insurance of its non-mobility. In addition, the area of greatest quantity of iron pipe and therefore mercury laden scale, the valve-pit area, required cleaning to restore it to service.

A chemical cleaning method was devised for the distribution valve area, based in part on generally used procedures for hot-water boiler cleaning and cleaning of metal surfaces in ship bilge areas. In order to evaluate the quantity of chemicals required and the need for removing scale, an Auger analysis was made of both sides of a carefully removed piece of scale. The iron oxide scale was typical, consisting of a magnetite layer (Fe₃O₄) separating the iron pipe from a porous surface coating of Fe₂O₃ (see Figure 5). The Auger

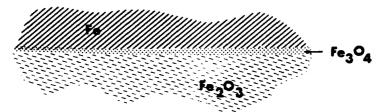


Fig. 5 - Model of iron oxide scale formed on surface of iron plumbing.

results and mercury analyses of a small section of the scale sample indicated that all mercury was contained in the outermost portion of the magnetite layer and the Fe₂O₃layer. Cleaning would therefore require little disruption of the protective inner magnetite coating. This result was confirmed by carefully separating portions of scale from both sides of a scale sample - only the exposed Fe₂O₃ surface contained appreciable amounts of mercury. A multi-step process was developed, beginning with acid-catalyzed chelation to remove the bulk of the mercury. The formulation chosen was a mixture of ethylenediaminetetraacetic acid (EDTA) and citric acid (H-Cit). Laboratory experiments using the removed section of 14-inch cast iron pipe allowed optimization of pH and concentrations. Citric acid and EDTA were chosen for two reasons. First, citric acid, acting as a general acid, can catalyze dissolution and complexation of hydrous iron oxides, thus increasing the rate at which mercury is liberated from the scale and available for complexing. Secondly, both citrate and EDTA have favorable formation constants for mercury(II) complexes compared to iron(II). The first formation constants are summarized in Table 1.

Table 1: Log of formation constants (K_1) for complexes of Hg^{2+} , Fe^{2+} and Fe^{3+} with citrate and EDTA (from references 10-12).

	log K ₁				
	Hg ²⁺	Fe ²⁺	Fe ³⁺		
citrate:	11.	4.4	11.		
EDTA:	22.	14.	25.		

The iron(III) formation constant is sufficiently high to insure its complete removal with the mercury. The lower formation constant for iron(II) and the inert nature of the magnetite layer would likely leave it intact. A scheme was devised to clean with the EDTA/citric acid mixture, follow with oxidation by chlorine of elemental mercury or mercury(I) left in the surface of the magnetite and clean again

with EDTA/citric acid to remove the oxidized mercury.

In preparation for this cleaning operation, valves were closed to isolate the entire distribution valve area and tower from the distribution system. Pressure was maintained in the distribution system by means of a surge tank attached to well no. 7 to avoid any back-flow of cleaning chemicals into the water supply. The setup operations uncovered a previously unknown "dirt leg" in the base of the tower which contained considerable amounts of mercury. In addition, portions of zinc sacrificial electrodes from the water tower contained as much as 0.1% mercury.

The EDTA/citric acid formulation devised was 125 lbs. Hampene NA3T (Na2HEDTA) and 100 lbs of citric acid in about 400 gallons of water heated to about 60°C while circulating through the system. This mixture gave the optimum final pH of 3.5 and still allowed fairly high concentrations of the EDTA. After cleaning with citric acid/EDTA, the system was flushed with water and treated with superchlorinated water (1 lb. Ca(OC1)2 in 400 gal) to oxidize any mercury(0) or mercury(I) to soluble mercury(II), and finally by another EDTA-citric acid treatment. The cleaning was monitored by mercury and iron analyses. The results are shown in Figure 6. Several important points are evident in these results: (1) The second EDTA-citrate treatment removed a proportionately much smaller amount of mercury, indicating that only a small portion was present as elemental mercury or mercury(I) and that the initial cleaning was very successful. (2) The chlorination did not remove iron (magnetite). (3) The total amount of mercury removed agreed fairly well with estimates based on mercury concentration in the scale samples.

After flushing the cleaned area, the tower and distribution valve area were returned to service.

Disposal of used cleaning solution must be considered very carefully. Available disposal options may indeed dictate the choice of cleaning methods. Regulations limiting the discharge of water containing high levels of heavy metals and the environmental impact of simple discharge of such wastes¹³ demand careful advance planning for proper disposal. In addition, recent literature implicating chelating agents such as EDTA in geological migration of heavy metals and radio-isotopes¹⁴, ¹⁵ require decomposition of this component to weakly or non-coordinating species. In the present case, the choices for proper disposal were quickly reduced to two options: (a) removal of mercury as precipitated sediment and slow discharge into the local sewage treatment system or (b) combustion with a scrubber-equipped high temperature incinerator. Either option would have been satisfactory. Cost of option (a) would have been considerably less, but would have

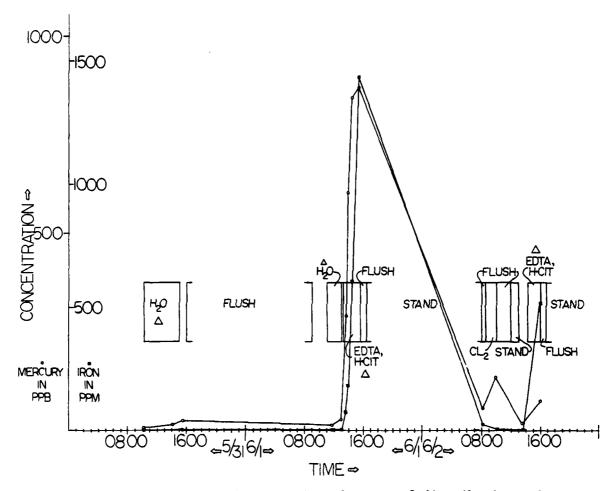


Fig. 6 - Iron and mercury analyses during clean-up of distribution value area.

to be done over an extended period of time to avoid swamping the bacteria in the tertiary system with EDTA. We were, however, relieved of the need for such a choice by individuals anxious to recover the temporary storage tank holding the waste. Acting in spite of impending plans for proper disposal, and in direct disregard for environmental consequences, these individuals discharged the waste cleaning solution onto the ground near the eastern shore of the Potomac River. Upon learning of this "spill" it was determined by consultation with local environmental authorities that no potable water intakes were present for several miles downstream of the discharge point and that the slow leaching into the river would not cause sufficient problems to warrent recovery efforts. This unfortunate incident should reinforce the need for careful advance planning for proper disposal.

The well, where high mercury concentrations indicated most of the mercury had gone, was cleaned by removing the inner 4-inch sleeve and pump and using an air-lift method to blow out the sediment and water in the well. Levels of mercury higher than 1% by weight were found in the scale inside the 4-inch inner pipe. It was therefore replaced. The pump, composed mostly of brass, was successfully cleaned with a dilute mixture of Na₃HEDTA and was returned to service. The debris and water removed from the well contained large amounts of mercury (as high as 14,000 ppb total). After the air-lift operation, levels of mercury in the well were down to 1.5 to 2.1 μ g/l and the well was subsequently returned to service after a two-month period of monitoring with levels consistently below 0.2 μ g/l.

Continued Monitoring. Results of analyses of the four monitoring points to mid-October, 1978 are shown in Figure 7. There is an approximately exponential overall decay of mercury in the system as reflected at these sampling points. The initial wide variations are likely due to the frequent flushing of the distribution system. Most other variations can be explained by analysis of the sampling conditions and provide important information regarding the uncontrolled variables in the sampling of such a system. The system as a whole remained well below the 2 μ g/1 EPA limit after October 1, 1978. Periodic monitoring was maintained for several months to insure the integrity of the water system as the restored well was brought back on line and to satisfy Federal analysis requirements for post-contamination situations.

SAMPLING PROBLEMS AND SCAVENGING OF MERCURY BY IRON OXIDES

The scavenging of mercury by iron oxide scale poses a complication to sampling. After finding that most of the plumbing leading from the main to the individual residences and inside the residences

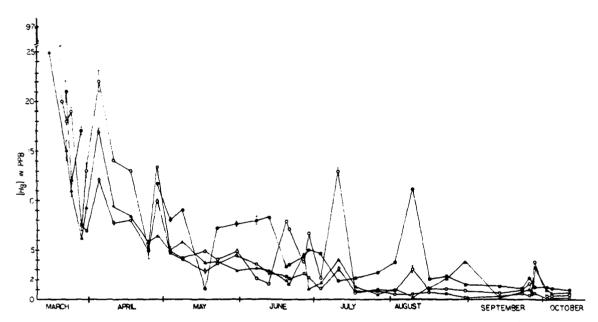


Fig. 7 - Mercury analyses at routine sampling points, quarters A (0), quarters I (\bullet), quarters W-3 (Δ), and bldg. 6 coffee mess (\Box).

was iron, it became apparent that some of the variations seen in Figure 7 were due to leaching of mercury from the scale into water standing in these pipes. The data beginning in mid-July reflect an attempt to control this variable by running the tap long enough before sampling to flush the local plumbing. A calculation indicated that two minutes should be adequate in all cases at full flow to flush the standing water and provide a representative sample from the main. Except for the results of Qtrs. I, which was undergoing plumbing repair during this period which presumably dislodged scale, this sample control seemed to provide results indicative of mercury concentrations in the system as a whole. It did mean, however, that considerable time would be required to remove by flushing the remainder of the mercury entrained in scale in the local plumbing.

This leaching of mercury from surfaces of iron plumbing also implies that for several samples on a given day, the minimum value should approach the bulk system mercury concentration. Therefore, it is likely that general trends in the system mercury concentration can be obtained from the earlier data by considering such a minimum value from several samples on a given day. It is assumed that the system variation is much smaller than the individual variations with length of time the water has been sitting in the local plumbing. Accordingly, Figure 8 shows the high, mean, and low values of the four samples at each date. Changes in the low value with time are considerably smoother than the fluctuations observed at any one location. There are some common fluctuations with the mean and high values, indicating some system variations. The above assumption of a wide local variation with time is supported by several experiments where sequential samples were collected at a given location. Figure 9 is typical of these results. There is always a substantial decline in mercury level as water is removed and the initial level is dependent on the length of time since the tap was last used.

The scavenging of mercury by iron oxide, was studied to determine the mechanism involved. Several different iron oxides from different sources were treated with solutions containing mercury. The experiment involved magnetite (Fe₃O₄) - both commercially available reagent and prepared from metallic iron and mild steel oxidized with air and HC1, and Fe₂O₃ from commercial sources and prepared by treatment of iron and mild steel with nitric acid. Samples of each of the above were treated with a real sample which contained 28 $\mu g/l$ Hg, a mercury(II) solution (1000 $\mu g/l$), tap water (less than 0.2 $\mu g/l$ Hg) and pure water. Without exception, the magnetite (Fe₃O₄) samples removed mercury from solution. The results were dramatic: excess Fe₃O₄ removes more than 90% of the soluble mercury, but Fe₂O₃ has little effect.

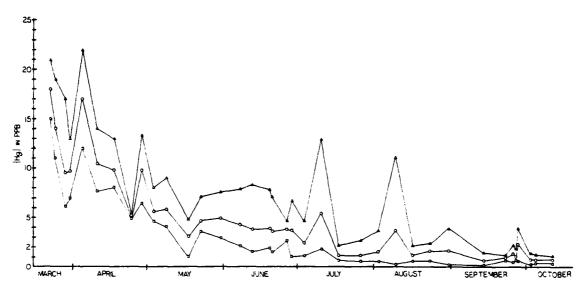


Fig. 8 - Mercury analyses at routine sampling points, highest value (Δ), mean (0), and lowest value (\square).

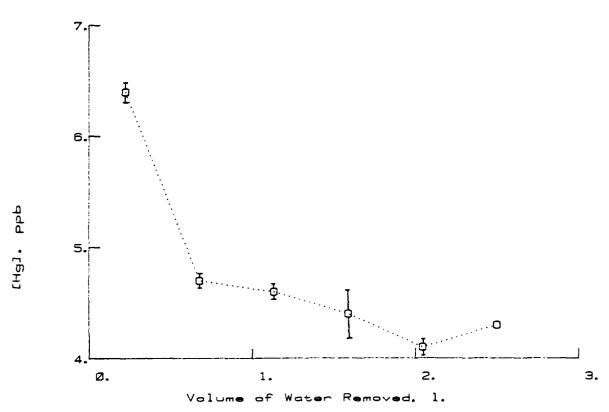


Fig. 9 - Mercury analyses of sequential samples collected at bldg. 6 site. (Error bars are $\pm \sigma$.)

It is possible that other materials such as precipitated carbonates are also involved in such processes, but clearly the magnetite is. Experiments with the entrained mercury in magnetite equilibrated with pure water and mercury-free tap water showed slow (minutes to hours) equilibration of the mercury, which is consistent with the observations of mercury levels in water standing in iron plumbing—both the local plumbing and laboratory experiments with the inner surface of the piece of 14-inch cast iron pipe. This slow equilibration also indicates that an ion-exchange mechanism may be involved in addition to or rather than reduction of the mercury(II). Such a phenomenon might usefully be applied as a filter for cleaning mercury from a polluted water supply.

A possible mechanism for transport of mercury within the water-Fe₂O₃-magnetite system involves reduction of the mercury(II) by iron(II):

(1)
$$2Fe^{2+} + 2Hg^{2+} \longrightarrow 2Fe^{3+} + Hg_2^{2+}$$
 $E^{0}=+0.149 \text{ V}$

(2)
$$2Fe^{2+} + Hg_2^{2+} \longrightarrow 2Fe^{3+} + 2Hg$$
 $E^{0=+0.018}$ V

Oxidation by dissolved oxygen or chlorine would readily cause the mercury to re-dissolve. In addition, presence of organic acids, amines, and chloride could alter the normally unfavorable reverse process,

(3)
$$2Hg + 2Fe^{3+} - 2Fe^{2+} + Hg_2^{2+}$$
 $E^{0}=-0.018 \text{ V}$

by the shifts in reduction and oxidation potentials that always occur with complexation.

Considerable recent work¹⁶⁻¹⁸ has quantified physical adsorption of mercury on hydrated Fe₂O₃, but no previous work was found implicating magnetite in such processes. Scavenging by iron(III) oxides and sulfides and some silicates are apparently responsible for reasonably low levels of mercury in normal surface waters¹⁹ and the ocean²⁰ as well as migration of mercury and other heavy metals within the environment.²¹ In the case of the sulfides, insolubility of mercury(II) sulfide is clearly the major factor¹³, and mercury(II) presumably binds to polymeric iron(III) oxides/hydroxides by simple complexation. Whether an ion-exchange process operates in the case of iron(II) and iron(III) oxides was not determined by our preliminary experiments.

An interpretation consistent with these observations can be made of the related sampling problem involving recycled sample bottles. Residual iron oxides remaining on the polyethylene surface from which

mercury has been removed by cleaning with nitric acid are then able to scavenge mercury from subsequent solutions. Entrainment of cations by such a mechanism is consistent with ion-exchange properties of many inorganic materials. 22

A final sampling problem involves the slow oxidation of elemental mercury by oxygen and perhaps by nitric-acid passivated polyethylene. Our initial experiments indicated that previous estimates²³ for the solubility of elemental mercury in water may be erroneously high. This would also complicate differentiation between oxidation states of mercury in real samples.

ACCURACY AND PRECISION

Accuracy of analytical results was assured by following standard and accepted methodology³ and by occasional determinations using a totally independent analytical method², particularly in the earlier analyses. The two methods were generally in agreement within 10% of the values obtained. The x-ray fluorescence method generally showed somewhat lower mercury concentrations than the cold vapor AA method. Using standard samples, it was determined that a slow loss of mercury occurred during x-ray fluorescence analyses and is presumed to be due to volatilization of elemental mercury by x-rays in the evacuated sample compartment.

Precision measurements were vigorously maintained through the resolution of the problem and into October of 1978. These efforts consisted of (a) multiple-operator correlations, which showed no significant variations, (b) repeated determination of standard curves, (c) standard addition experiments to allow estimate of lower detection limits using real samples, (d) dilution experiments with samples having mercury concentrations near 10 µg/1, and (e) replicate analyses. Replicate sampling and significance testing (Student's test) demonstrated (a) the leaching of mercury from scale described above and shown in figure 9, (b) the non-uniformity of the distribution system both temporally and spatially, and (c) inhomogeniety of six early high level samples near pump house 6 -- repeated analyses with more vigorously homogenized samples and care in dilution eliminated this problem.

That volumetric errors contributed no systematic error and that precision followed a relationship to concentration usual for chemical analyses $^{24-27}$ is shown in figure 10. Least-squares lines for data with no dilution (slope=0.0042 \pm 0.006), samples diluted 1:2 (slope=0.019 \pm 0.004) and samples diluted 1:10 (slope=0.036 \pm 0.02) show the expected increase in slope with concentration. Data where significant particulates or elemental

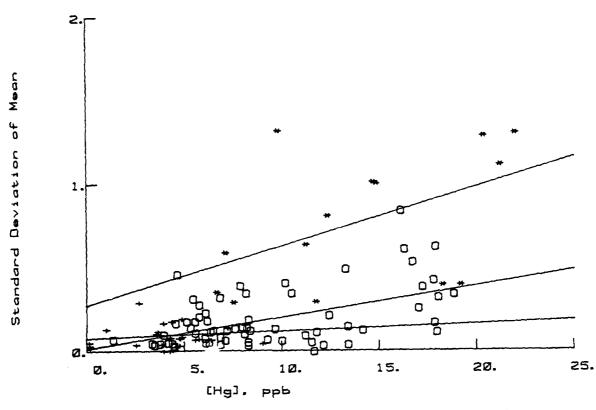


Fig. 10 - Analytical precision as a function of concentration. *=1:10 dilution, 0=1:2 dilution, +=no dilution.

mercury was present in the sample were excluded from this analysis. To a first approximation, standard deviation (σ) was a linear function of concentration within one dilution range. Of course, the usual definition of detection limit²⁸ requires that σ become much higher relative to concentration as one approaches the detection limit. That such a result is not seen here is due to (a) few data near the detection limit and (b) a likely true detection limit below the value determined by standard addition experiments. Figure 11 shows variation of standard deviation as a function of mercury concentration for the two different instruments used for undiluted samples. Least-square lines show some differences (lower line for P.E. 460). The single-beam Perkin-Elmer 272 is clearly less stable in spite of more frequent calibration. Results, however, were still within the approximately 10% error range.

Mean mercury concentrations for samples taken through October of 1978 are tabulated in the appendix. Following October, replicate runs were generally reduced to two analyses per sample and all results were well below the 2 μ g/l Interim Standards requirement.

CONCLUSIONS AND RECOMMENDATIONS

It is clear that malfunctioning or incorrectly installed mercury-containing water flow meters in use in public drinking water systems pose a significant threat to health. It is also clear that the time and expense involved in correcting a mercury spill of this sort is significant. It is recommended that water supplies using mercury flow meters of this sort insure that they are correctly installed, that regular mercury analyses be performed, and that no mercury be added to such meters without suspecting loss into the system and determining its destination.

A simpler solution is to remove these meters altogether. It is likely that sufficiently accurate flow measurements can be obtained with other devices or by monitoring the time that pumps are running.

The presence of iron oxide scale in plumbing systems can have a significant impact on the accurate diagnosis of a mercury contamination problem, and more importantly, can serve as a mercury buffer, resulting in a lower system concentration and minimizing the health impact.

Finally, proper disposal of waste cleaning solutions containing mercury or EDTA is very important. Simple discharge into the environment is unsatisfactory from the standpoint of mercury pollution or the migration of heavy metals or radioisotopes which the EDTA would cause. In the case described here, proper disposal by (a)

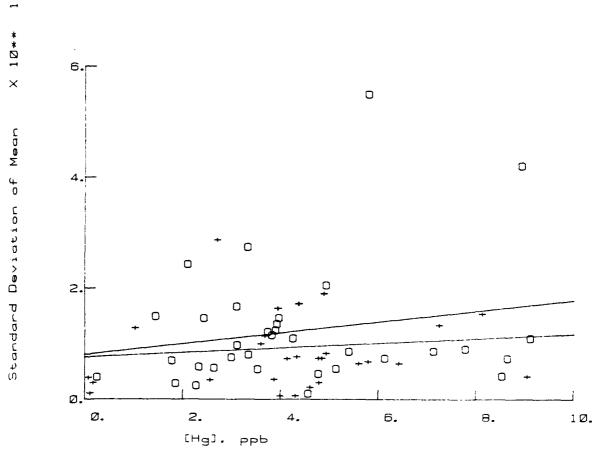


Fig. 11 - Analytical precision as a function of concentration for two instruments used. P.E.460 is lower least-squares line (+), P.E.272 is upper least-squares line (0).

removal of mercury as precipitated sediment and slow discharge into the local sewage treatment system or (b) combustion with a scrubber-equipped high-temperature incinerator was obviated when individuals aware of the potential risks involved dumped the waste solution on the ground near the Potomac River.

ACKNOWLEDGMENT

We are deeply indebted to Robert Conlyn, Station Engineer at Chesapeake Bay Division, NRL, without whose careful study of the missing mercury situation this problem would not have come to light and without whose patience and engineering expertise it could not have been resolved. Cooperation from Duane A. Geuder, Gabe Lapidus and J. Dakita of the District of Columbia Department of Environmental Services in the form of the loan of considerable amounts of reagents in short supply is gratefully acknowledged. Assistance from John F. Murray and Robert L. Shuler, who performed some of the nearly two thousand individual mercury analyses, was greatly appreciated.

APPENDIX

	LE	•	SAMPLE	CONHENTS
ÛATE	NO.	(PPB)	LOCATION	
nja gar estretja est est			es ministra	an states, control systems
3-10-78	i	97(30)	Qtrs A cu	
3-15-78	i	25(19)	Atrs B cu	
	2	20,2iss	Atrs J grape Koolaid	
	3	25(19)	Bldg 5 coffee mess	
3-20-73	í	i,	Emergency supply	(6 years old)
		20(12,(1.355)		
		10(10,(1.355)		
	4	20(15,(1.3ss)	Qtrs J cw	
	5	1(3,3,(1,355)	Pump House 7	
3-22-78	i	18	Qtrs A cu	
		21	ijtns I cu	
		12	Qtrs ¥13 cu	
		i 5	Bldg 6 coffee mess	
			Pump House 7	
		(9)	Pump House 6, check side	
		(54)	Pump House 6, well	
	g	7.9	"Hollow" area	(old water)
3-24-78	-	19	Utrs A cw	
	2	12	ütrs I cu	
	3	8	Atrs W13 cw	
	4	ii	Bldg 6 coffee mess	
	5	(.2	Pump House 7	
		(208)	Pump House & check side	
		(93)	Pump House & well	contained Hg droplets
		₹.2	NRL 207/313 CW	
		7.7	Tower before flush	
	B,C	5(.3)	Tower sludge	
3-28-78	1	7.4	litrs A cu	
	2	13	Otrs 8 cu	
	3	17	atrs C cu	
	4	10	Atrs D cu	
	5	18	Utrs E cw	
	6	19	atrs F cu	
	7	9.7	Atrs G cu	
	8	13	Qtrs H cu	
	9	i 7	ûtrs I cu	
	11)	9.0	Utrs J cu	
	11	6.0	Atrs Wi cu	
	12	ó.7	ütrs W2 cu	
	13	7.5	Utrs W3 cw	

SAM	PLE	Hg	SAMPLE	COMMENTS
DATE	NO.	(PPB)	LOCATION	

	14	7.2	atrs 44 cu	
	15	4.5	Atrs WS cu	
	iò	4.7	Qtrs W6 cw	
	17	3.3	Utrs W7 cu	
	13	8.3	Gtrs W8 cw	
	19	5.6	Qtrs W9 cw	
	20	11	Qtrs W10 cu	
	21	3.2	Utrs Wii cw	
	22	7.1	Qtrs W12 cw	
	23	10	Utrs W13 cu	
	24	ii	Qtrs WiS cu	
	25	6.1	Bidg 6 Coffee Mess	
	25	.2	Store, Randales Cliff	
	27	(272)	Pump House 6 sample tap	contained Hg droplets
	23	(,2	Pump House 7 sample tap	
	2 9	(.2	Bay water at pier	
	30	19	Qtrs A hu	
	31 72	17	Qtrs 8 hu	
	32 77	8.3	Qtrs C hw	
	33	5.2	Otrs D hu	
	J4	3.5	Qtrs 41 hu	
	35	(4.5)	Utrs W2 hu	
	36 37	52	gtrs W3 hw	
	28	15(13) 18(4.2)	ijtrs W4 hw Qtrs W5 hw	
	39	86(5.0)	itrs 46 hu	
	3. 48	101(6.7)	Qtrs W7 hw	
	41	32(5.0)	Qtrs W8 hw	
	12)1500(14)	Qtrs W9 hw	
	43	57(1.2)	Atrs W10 hu	
	14	84(4.2)	Qtrs Wii hw	
	45	(2.1)	Qtrs W12 hu	
	16	224(5.2)	Qtrs Vi3 hw	
	47	232	Qtrs W15 hw	
	A	(.2	Atrs A outside tap	Overlook Ave
	••	``-	2.1.5 11 0013300 149	012.101.111
3-30-78	i	151	Hydrant at Whirling Arm	
	2	(67)	Pump House 6 Well	
	3	⟨.2	Pump House 7	
	4	5.9	Otrs W3 cu	
	5	13	gtrs A cw	
	દ	9.3	Bidg 5 coffee mess	
	7	(5.3)	Pump House 5 upper tap	
	8	.3	81dg 4 ice cubes	spec 1 (3/20)
	7	i	Bldg 4 ice cubes	spec 2 (3/28)

SAM	PLE	Hg	SAMPLE	COMMENTS
DATE	NO.	-	LOCATION	
			******	*****
	10	۶,	Bldg 75 ice cubes	spec 1 rm 308 (3/28)
	ii	(,2		spec 2 (3/28)
	12	(.2		spec 3 (3/29)
		(.2		spec 4 (3/29)
	14	()1290)		sediment: contained Hg droplets
	••	1/2200/	1300 gua 1400 0000	January Constants in a space
4-04-73	í	22	Qtrs A cw	
7 47 70	2	28	Atrs J cu	
	3	12	Qtrs W3 cu	
	4			
		17	Bldg & coffee mess	
	5	.7 .	Pump House 7 sample tap	
	6	26	Pump House 6, well	
4-10-78	ì	14	Qtrs A cw	
	2	18	Atrs J cu	
		7.7	Atrs N3 cu	
	4	9.4	Bldg & coffee mess	
		1. 2	Pomp House 7	
	6	248	Pump House 6, well	
	7	30(9.6)	· · · · · · · · · · · · · · · · · · ·	
			Atrs A hu	
	8	9.6	Qtrs B hw	
	3	14	Qtrs C hu	
	10	6.6	Atrs D hu	
	ii	16	Atrs E hu	
	12	13	Qtrs F hw	
	13	i S	gtrs G hu	
	14	18	Qtrs H hw	
	15	31	Qtrs I hu	
	15	ii	Qtrs J hw	
	17	5.9	Gtrs Wi hw	
	i 8	6.5	Otrs W2 hw	
		4.6	Utrs 43 hu	
	29	6.9	Qtrs 94 hw	
	21	3.4	litrs WS hu	
	22	5.9	Qtrs W6 hw	
	23	5.1	Otrs W7 hw	
	24	6.3	Qtrs W8 hu	
	25	10	Qtrs W9 hu	
	26		•	
		8.2	Gtrs Will hu	
	27	12	Qtrs Wii hw	
	23	5.4	Otrs W12 hw	
	29	5.2	Qtrs W13 hw	
	28	8.1	Atrs W15 hw	
4-17-73	1	13	Utrs A cu	

SAMP	LE	Hg	SAMPLE	COMMENTS
DATE	NO.	(PPB)	LOCATION	

		10	Name 7 min	
	2	12	Utrs J cu	
		8.3	Otrs W3 cu	
		8.4	Bldg 6 coffee mess	
		1.4	Pump House 7	
		330	Pump House & sample tap	
		51	Pump House 6 sample tap	-
	3	51	Pump House & boiler drai	n
	3	ii	open tank bottom drain	
	A	[.026]	Open Tank, sediment	as mg Hg / g of sediment(sand)
4-20-78	ń	[.019]	Open Tank, Sediment	as mg Hg / g of sediment(sand)
4-21-79	1	22(13)	14" cast-iron pipe	after breaking
	2	408(70.)	bottom of 14" valve	after removing Tee
		460	bottom of 5" valve	tower side of 14" valve
	À	[.54]	Main TEE scrapings	(from Fox)
		•		
4-24-78	i	4.8	Qtrs A cw	
		5.0	Strs W cu	
	:	3.3	Qtrs J cw	
	4		Bldg & coffee mess	
		224(100)	Pump House 6 sample tap	
		31(20)	Pump House & sample tap	
	?	343(96)	Pump House 6 open tank	
	ė	.2((,2)	Pump House 7 sample tap	
	9	392(11.)	14° transite line	
	-			
4-25-78	1	5.6	Bldg 6 coffee mess	time=0800
	2	5.6	Bldg & coffee mess	tine=0900
	3	4.4	Bldg 6 coffee mess	time=1000
	4	4.5	Bldg & coffee mess	time=1130
	5	4.0	Bldg & coffee mess	time=1200
	6	6. i	Bldg 6 coffee mess	tine=1300
	7	5.6	Bldg 6 coffee mess	time=1400
	3	4.2	Blag 6 coffee mess	time=1508
	9	2.5	Bldg 6 coffee mess	time=1600
4-28-73	1	6.4	Bldg 6 coffee mess	sample 1
	2	4.7	Bldg & coffee mess	sample 2
	3	4.6	Bldg 6 coffee mess	sample 3
	4	4.4	31dg & coffee mess	sample 4
	5	4.1	Bldg 6 coffee ness	sample 5
	5	4.3	Bldg & coffee mess	sample ó
	7	9.9	etrs A cu	ample v
	8	13.4(8.4)	Qtrs 43 cu	
	9	11.7	Qtrs I cu	
	7	41.7	ASLA T FM	

HAS	PLE	Hg	SAMPLE	COMMENTS
DATE	NO.	(PP3)	LOCATION	
	4.6			
		6.2(4.9)	Pump House 6, open tank	
	11	.20(.26)	Pump House 7	
5-3-78	i	4.8	Atrs A cu	
		3.0	Qtrs I cu	
		4.6	Atrs W3 cu	
		4.9	Bldg & coffee mess	
		(.2((.2)	Pump House 7 sample tap	
		15000(350)	Pump House 6 sample tap	at start up
		74(68)	Pump House & sample tap	
	3	26(19)	Pump House & sample tap	
	9	15(10)	Pump House 6 sample tap	
	10	27(15)	Pump House 6 open tank	TO HER GIVES STORY OF
		4. (82)	roop noose o open tonk	
5-8-78	i	4.2	gtrs A cu	
	2	9.0	Qtrs I cw	
	3	4.0	Qtrs W3 cw	
	4	(.2((.2)	Pump House 7 sample tap	
	5	5.8	Bldg 6 coffee mess	
	5	86	•	at start-up
	7	ii		after 2 min
	ર	ii	Pump House 6	after 4 min
	7	3.8(4.4)	Pump House &	after 10 min
	18	4.3(3.2)	Pump House 6 open tank	
	11	(35)	Pump House & open tank	sand and sediment
5-17-70	í	4.3	Atrs A cu	
3-11 /4		1.8		•
	3	2.8	Qtrs I cu	
	1	3.7	Otrs W3 cw	
	5	3./ (.2	31dg & coffee mess cu	
	5	96(34)	Pump House 7 sample tap	## #### - ##
	3	70(34)	Pump House & sample tap	at start-up
5-22-73	i	4.3	Qtrs A cw	
	2	7.2	lites I cu	
	3	(.2	Pump House 7 sample tap	
	4	3.6	Qtrs W3 cu	
	S	3.8	Bldg & coffee mess	
	ક	63(31)	Pump House & sample tap	at start up
5-30-73	1	4.3	litrs A cu	
		7.6	Atrs I cu	
		⟨.2	Pump House 7 sample tap	
	4	4.4	Atrs W3 cu	
	5	2.9	Bldg & coffee mess	
			-	

SAM	PLE	Hg	SAMPLE	COMMENTS
DATE	NO.		LOCATION	
	5	127	Pump House & sample tap at	start-up
				- · · · · · · · · · · · · · · · · · · ·
5-31-73	i	7.9	Hot water, before pumping i	nto system
	2	i3.2	Sample tap off standpipe	in pit
	3	21.9	From 400 gallon tank	•
	÷Α	70	Liquid over sludge in 4' :	iser
	4B	[.024]	Sludge from 4' riser	
	5	[.0056]	From 8" into 4' riser slu	ige
	Rod	[.083]	Dry encrustation from Zn r	
			•	
5-1-73	1	12.4	400 gallon tank hu	
	2	24.1	400 gallon tank before ED	TA added
	3	260	400 gallon tank at 13:40	
	4	598	408 gallen tank at 13:55	
	5	78 5	400 gallon tank at 14:30	
	Ł	[.00035]	Bottom of 4' riser	
	7	[.20076]	1.5' from bottom of 4' ris	
	ន	760	400 gallon tank at shotdoo	wn,15:35
5-2-78	i	56	Sample from 3° drain at 00	3.40
0-2-70	2	41.2	Sample from 8° drain at 08	
	3	36	Sample from 3° drain at 08	
	1	17	Dirt leg" at base of tank	
	Š	146	Superchlorinated	
	5	20	14° riser after chloring	tian the sace
	7	5i	400 gal tank after 2nd cli	ilonjine rest Nan-un u/ EBYA/eithate
		[.0040]	Sand from bottom of 4' ris	
		[.023]	Outside scrapings from 14	
	19	(.023)	Outside scrapings from 14	
		[.889]	Inside scrapings from 4';	
		[.0011]		set
	13	[.0028]	4	iet
	••		229 11 010 21 12201	
5-5-78	í	14	Discharge from 8° drain	
	2	9	³' standpipe	
	3	31	i" valve in pit	
6-6-78	1	6.4	Holding tank after 10 min	
	2	5.5	4' dirt leg after sitting	
	j	3.6	14° riser after sitting o	ern14
6-7- 78	1	3.4	Bottom of 4º riser	
	2	2.6	14° riser	
	i	3.3	Gpen tank (480 gal. tank?)
	4	4.8	Qtrs.W-3, cu	
			•	

SAM	PLE	Hg	SAMPLE	COMMENTS
DATE	₩0.	(PPB)	LOCATION	

	S	7.9	Qtrs.I, cw	
	5	3.2	Bldg #6 Coffee m	ess
		2.1	Qtrs.A, cw	
	8	.2		aple tap at start-up
	•		i subuenze er)	ilban tab at at at the
6-12-78	1	[.95]	Down end of "T" at	top of well
	3	[15.9]	Bottom of 1st pipe	section, inside
	5	[11.1]	Bottom of 2nd pipe	
	Š	[.017]	Bottom of 2nd pipe	section, outside
	Ü	[10.7]	Bottom of 3rd pipe	section, inside
	10	[13.0]	Bottom of 4th pipe	
	i 2	[7.3]	Bottom of 5th pipe	section, inside
	14	[5.0]	Bottom of 6th pipe	section, inside
		[6.8]	Bottom of 7th pipe	section, inside
	i 7	[.067]	Bottom of 7th pipe	section, outside
	19	[3.7]	Bottom of 8th pipe	
	21	[5.9]	Bottom of 9th pipe	section, inside
	22	[7.8]	lop of 10th pipe s	ection, inside
	23	[7.2]	Bottom of 18th pip	e section, inside
		15.91	Bettom of 10th pip	e section, inside cufflink
	25	[10.5]	Top of 11th pipe s	ection, inside
	2."	1.0651	Intake screen debr	is & around joint
	23	[.46]	Intake screen debr	is & around joint
		1.561	Inside check valve	l .
	20	[.23]	Top end of pump pi	
		2.9	Blog.#6, Coffee m	1655
		629	Pumphouse #6 at st	art-up, sample tap
		2.7	ÿtrs.¥−3, cw	
	ĴΫ	3.3	ütrs.I, cw	
		140	Pumphouse #6, Samp	le tap 6 min after start-up
	36	1.45	iltrs.A, cu	
	37	₹.2	Pumphouse #7, Samp	sle tap at start-up
6-13-78		. •	N-4 1146	is summa before Clumbian
0-13-/8	1 2	68		ors in pump before flushing
	-	129	Start of pump flus	
	3	28		gal tank after initial flush
	1	210		m pump-ist flush (Test \$2)
	5	100	EDTA poured throug	
	\$	1.8	1500 gat tank fina	il drain-off out of pump
6-14-70	ı	38	Vell blow-out, i m	in after start
_		82(14)	Well blow-out at (
	2 3	188(35)	Well blow-out at 0	
	4	808(180)	Well blow-out at 6	
	5	170(11)	Well blow-out at 0	
	-	_, .		· · ·

SAM	PLE	Нg	SAMPLE COMMENTS
DATE	NU.	(PPS)	LOCATION

	6	66(20,4)	Well blow-out at 09:57 Last sample
	_		444 444
6-15-78			Well blow-out at ii:ii
		119(1.8)	Hell blow-out at 11:17
		2400(140)	Well blow-out
		60(27)	Well blow-out at 13:02 (Resumed at 12:57)
		1394(206)	1508 gal tank, Horning's accumulation
	A	[.0096]	Scrapings from well casing, 509' depth & up
5-15-78	4	430(1.0)	Air jet at 525' level at start of pumping
• 10 /0		12308(40)	"Bottom load" 3 min after start of pumping
		20(6.2)	20 min after start of pumping, running clear
		750(59)	Composite from drain of 1500 gal tank
	à	[.078]	
	a	1.0/01	Sludge from 1500 gal tank from 6-15 air pumping
6-19-78	í	3.3	Utrs. I cw Sudsy
		7.9	itrs.A cw
		2.3	Qtrs.W-3 cw
		3.5	Pump House 7 Sample tap at start-up
		1.9	Eldg. #6 coffee mess
		2560	From lower drain, 1500 gal tank after 1/2 full
	_	.55	Filtrate from 6-19-78 \$6
		[.50]	Solids from 6-19-78 \$6
		53(40.)	Last water from hose at 528' level
	á	34(1.6)	From S31' level
	•	3711.07	LLAM 221. ISASI
6-20-78	1	1348(284)	Well filled back from 535'-532', top of fill
	2	3.5	Qtrs.I cw
	3	7.i	ûtrs.A cw
	4	2.1	Otrs.W-3 cu
	5	(.2	Pumphouse \$7 Sample tap
	٤	1.5	Bldg. #6 coffee mess
	7	20.0	Hell depth of 537' at 08:43
	8	25.6	Well depth of 538' at 09:01
	7	24.6	Well depth of 539' at 09:31
	10	25	Well depth of 542' at 19:08
	1 i	1.7	Well depth of 535' before pumping stopped @ 17:00
6-21-78		40 A	
9-51-19	1	18.4	From EDTA holding tank
	2	26.2	From EDTA holding tank
	5	140	From pump cleaning EDTA soln. 8 11:45
	4	128.	From pump cleaning EDTA soin. # 12:45
6-22-78	i	5.3	Drawn from screen
	2	1.2	Disconnected from lead packer-Drawn from well as a whol
		•	

SAM	PLE	Hg	SAMPLE	COMMENTS
DATE	Ю.	•	LOCATION	
6-26-73	i	2.6	Qtrs.W-3 cu	
	2	1.2	Pumphouse \$7 Sample tap	
	3	3.8	Atrs.A EW	
	4	4.3	Qtrs.I cu	
	5	4.5	Bldg. #6 coffee mess	
6-27-73	i	38	From "dirt leg" at base	of riser (400 kG tank)
5-28-73		2.2	Qtrs. U -3 cu	
		(.2	Pumphouse \$7 sample tap	P
		6.7	Qtrs.A Cu	
	4	4.9	Qtrs.I cu	
	ζ	.96	Bldg. \$6 coffee mess	
7-3-78	i	1.1	Qtrs. W-3 cw	
		(.2	Pumphouse \$7 sample to	0
		2.2	Qtrs.A cw	•
		4.6	Qtrs.I cw	
	S	1.7	Bldg.#6 coffee mess	
7-6-78	i	8.14	Pump-washing tank prior	to pump innersion
7-7-78	i	3.1	Pump-washing tank after	pump soaked
7-10-78	4	3.0	gtrs. II-3 cu	
7-10 /4		.31	Pumphouse #7 sample to	n
		12.7	Atrs.A cw	Υ
	4	1.3	ätrs.I cw	
	Š	4.8	Bldg.#6 coffee mess	
7-17-78	4	.33	Utrs. N-3 cu	
1-11-10		(,2	•	(black cond in basela)
	3		gtrs.A cw	(black sand in bottle)
	ن ‡	. 5 2.1	etrs.i cu etrs.i cu	
	5			
	•	1.3	Bldg.‡6 coffee mess	
7-26-78		1.1	gtrs. W-3 cu after 2 mi	
	2	4.2	Pumphouse \$7 sample tap	
	3	1.0	igtrs.A cu after 2 nin.	
	1	2.9	Qtrs.I cw after 2 min.	
	5	.7	81dg.#6 coffee mess aft	ier c min.
8-2-78	i	.7	Qtrs. N-3 cw after 2 min	iutes
	2	⟨.2	Pumphouse #7 sample tap	after 2 min.

SAM	PLE	Hg	SAMPLE COMMENTS
DATE	NO.		LOCATION
	3	1.01	Qtrs.A cw after 2 minutes
	_	3.9	Atrs.1 cw after 2 minutes
	5	i.i	
	3	1.1	Bldg.#6 coffee mess after 2 min.
3-9-7 3	i	، هٔ	Atrs. 4-3 cw after 2 minutes
	2 3	₹.2	Pumphouse #7 sample tap after 2 min.
	3	3.0	Atrs.A cw after 2 minutes
	4	11.1	Utrs.I cw after 2 minutes
	5	.2	Bldg.#6 coffee mess after 2 min.
8-15-78	i	5.7	Qtrs.W-3 cw First water
0 10 /0	2	.7	Atrs. N-3 cw after 2 minutes
	3	(.2	Pumphouse \$7 after 2 minutes
	4	1.5	- · · · · · · · · · · · · · · · · · · ·
	5	i.i	Atrs. A cw First water
		5.i	Atrs. A cw after 2 minutes
	8 7	2.2	Otrs. I cu First water
			Atrs. I cw after 2 minutes
		3.7	Bldg. #6 coffee mess First water
	9	1.2	Bldg. #6 coffee mess after 2 minutes
3-23-78		۶.	Atrs. 4-3 cw after 2 minutes
		(.2	Pumphouse #7 after 2 minutes
	3	i. i	Atrs. A cw after 2 minutes
	4	2.4	Atrs. I cw after 2 minutes
	5	2.2	Bldg. #6 cw coffee mess after 2 minutes
8-30-78	4	0.2	Qtrs W-3 cw after 2 min.
0 00 70	-	⟨.2	Pump House 7
		,9	Qtrs A cw after 2 min.
	4	1.5	Utrs I cw after 2 min
	5	3.3	Bldg 6 coffee mess cu after 2 min.
		.=	•
9-1-78	1	156(129)	Pump House 6 well bottom sample
9-6-78	:	808	Pump House 6 blow-out sample 1
	2	1.1	Pump House & blow-out 2 min
	3	3.8	Pump House & blow-out at 4 min
	4	2.1	Pump House 6 blow out at 10 min
9-7-79	í	٠,5	Pump House 6 2nd blow-out 3 min
. ••	2	1.1	Pump House 6 2nd blow-out 2 min
	3	11.9	Pump House 6 2nd blow-out 4 min
	4	⟨.2	Pump House 6 2nd blow-out 10 min
			·
9-8-79	i	.7	Pump Heuse 6, pump en 37 min

SAME	'LE		SAMPLE	COMMENTS
DATE	NU.		LOCATION	
			-8 win a 10 m	
	2	i.4	Pump House 6, pump on 10 min	
		11.6	Pump House 6, pump on 4 min	
	4	1.9	Pump House 6, pump on 2 min	
	5	6.8	Pump House 6, pump on 0 min	
	6	. 6	Pump House 5, pump on 1 hr	
	7	1.3	Pump House 6, pump off 4 hr, on	iO min
9-9-78	i	18.4((.2)	Pump House & at 0 min	
		5.1((.2)	Pump House 6 at 2 min	
	3	1.1((.2)	Pump House 6 at 4 min	
		.8	Pump House 6 at 10 min	
	5	₹.2	Pump House 6 at 8 hr	
9-11-78			Pump House 6 at 0 min	
		5, i	Pump House 5 at 2 min	
	3	.7	Pump House 6 at 4 min	
	4	.3	Pump House 6 at 18 min	
9-12-73		1.9	Pump House 6 at 0 min	
		6.6	Pump House 6 at 2 min	
	3	2.1	Pump House 5 at 4 min	
		.3	Pump House 6 at 18 min	
	ל	₹,2	"stream fall"	
9-13-78	1	1.3	* Pump House 6 at 0 min	
	2	1.7	Pump House 5 at 2 min	
	3	.3	Pump House & at 4 min	
		(.2	Pump House 6 at 19 min	
		.3	Pump House 6 at 4 hr	
		₹.2	"stream fall"	
		.2	Qtrs #-3 cw after 2 min	
	3	.2	Pump House 7 after 2 min	
	9	.7	ûtrs A cw after 2 nin	
	10	1.4	Otrs I cw after 2 min	
		₹.2	Bldg 6 cw Coffee mess after 2 m	HB
	12	.3	Pump House 6 after 4 hr	
9-14-78	i	(.2	Pump House 6 at 9 min	
	2	(.2	Pump House 6 at 1 min	
	3 4	.5	Pump House 6 at 2 min	
	5	(.2	Pump House 6 at 3 min Pump House 6 at 4 min	
	5	⟨.2 ⟨.2	•	
	7	1.2	Pump House 5 at 10 min Pump House 6 at 1 hr	
	8	\.2 \.2	"stream fall"	
	0	116	Sileau Latt	

SAMPLE			SAMPLE COMMENTS
DATE	NO.	(PPB)	LOCATION
0 40 70		47.0	Book Norway / An All min
9-13-78		13.V .3	Pump House 6 at 4 min Pump House 6 at 1 min
		(.2	Pump House 6 at 2 min
		2.3	Pump House & at 3 min
		⟨.2	Prep House & at 4 min
		(.2	Pump House 6 at 10 min
9-20-78	i	1.3	Pump House & Boiler drain at 0 min
, 40 , 0		2.9	Pump House & Boiler drain at 2 min
		3.6	Pump House & Sample tap at 0 min
		7.8	Pump House & Sample tape at 2 min
		2.2	Pump House 6 Sample tap at 4 min
		1.3	Pump House & Sample tap at 10 min
9-21-78	i	1.8	Pump House & Sample tap at 0 min
	2	1.6	Pump House 6 Sample tap at 2 min
	3	(.2	Pump House & Sample tap at 10 min
	4	(.2	Pump House & Sample tap at 20 min
		⟨.2	Pump House 6 Sample tap at 2 hr
9-22-78	i	.6	gtrs W-3 cw at 2 min
	2	1.9	Pump House 6 sample tap at 2 min
	3	1.0	Utrs A cw at 2 nin
		1.2	Atrs I cw at 2 min
	ţ	.8	Bldg 6 coffee ness cw at 2 nin
9-25-78	1	1.6 2.2 .45	itrs A cw at 2 min
	2	2.5	Atrs I cw at 2 min
	3	.45	Atrs N-3 cu at 2 min
	ŧ	1.0	Bldg 6 coffee ness cw
		2.2	Pump House 6 at 2 min
	á	₹.2	"Stream fallout" 100 feet from bay
9-26-78	i	.65	Itrs A cu at 2 min
		1.3	Atrs I cu at 2 min
	3	.79	Atrs W-3 cw at 2 min
	4	.7	Bldg 6 coffee mess cw at 2 min
	5	.36	Pump House 5 at 2 min
	6	(.2	"Sample stream, 100 ft."
9-2 7-7 8	i	3.8	Atrs A cu at 2 min
	2	1.3	Atrs I cw at 2 min
		.6	Atrs 4-3 cm at 2 min
		3.2	Bldg 6 coffee mess cw at 2 min

SAMPLE		Hg	SAMPLE	COMMENTS
DATE	жu.	-	LOCATION	
	5	.2	Pump House 6 at 2 min	
13-2-78	i	.4	Qtrs A cw at 2 min	
		1.3	Otrs I cu at 2 nin	
		.2	Atrs W-3 at 2 min	
		1.0	Bldg & coffee mess cw at 2 min	
		.7	Pump House 5 at 2 min	
10-4-73	i	.4	Qtrs 6 cw at 2 min	
		1.2	Atrs I cw at 2 min	
		.35	Qtrs W-3 cw at 2 min	
	4	.5	Bldg 6 coffee mess cw at 2 min	
	5	i.0	Pump House 6 at 2 min	
10-11-78	í	.5	Qtrs A cw at 2 min	
	2	1.0	Ates I cw at 2 min	
	2	.3	Qtrs W-3 cw at 2 min	
	4	.8	31dg 6 coffee ness cw at 2 nin	
	5	.7	Pump House & sample tap at 2 mi	

OTES:

ppb = parts per billion (micrograms per liter of sample)

ss = suspended solids

cw = cold water (in residences, from kitchen *

hw = hot water (from drain on water heater)

spec = specimen

- () indicate analyses performed by x-ray fluorescence
- () indicate results for supernatant liquid only (does not include suspended solids)
- l lindicate analyses of solid samples and are reported as mg of mercury (total) per g of solid

REFERENCES

- 1. A preliminary report of this project was presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 5, 1979.
- 2. For description of x-ray fluorescence analysis methods see R. Panayappan, D. L. Venezky, J. V. Gilfrich, and L. S. Birks, "Determination of Soluble Elements in Water by X-ray Fluorescence Spectrometry after Preconcentration with Polyvinylpyrrolidone Thionalide," Anal. Chem., 50, 1125 (1978).
- 3. "Mehtods for Chemical Analysis of Water and Wastes," EPA-625-6-74-003 Washington, D.C. (1974).
- 4. See for example Robert Klein, Jr. and Clifford Hach, Am. Lab., 9, 21 (1977).
- 5. We are indebted to James S. Murday of Surface Chemistry Branch, NRL, for performing Auger measurements on scale samples.
- 6. "Primary Drinking Water, Proposed Interim Standards," Federal Register, 40 (51), 11990, March 14, 1975.
- 7. William F. Fitzgerald, <u>Limn</u>. and <u>Ocenog</u>., <u>20</u>, 468 (1975).
- 8. Herbert V. Weiss, Thomas E. Cozier, Anal. Chim. Acta, $\underline{58}$, 231 (1972).
- 9. Performed by J. Wright, Naval Environmental Health Center, Cincinnati, Ohio using cold vapour AA methods described in P. and C.A.M. No. 165 for Urine, Vol. 1 (NIOSH).
- 10. L. G. Sillen and A. E. Martell, "Stability Constants of Metal-ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.
- 11. L. G. Sillen and A. E. Martell, "Stability Constants of Metal-ion Complexes, Supplement No. 1," Special Publication 25, The Chemical Society, London, 1971.
- 12. A. E. Martell and Robert M. Smith, "Critical Stability Constants," Vol. 3, Plenum, N. Y., 1977.

- 13. R. P. Eganhouse, J. N. Johnson, D. R. Young, and D. J. McDermott, "Mercury in Southern California Waters: Inputs, Distribution, and Fate," Summary Rpt., 1971-75, SCCWRP-TM227-76.
- 14. Jeffrey L. Means, David A. Crerar, and James O. Duguid, Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents, Science, 200, 1477 (1978).
- 15. Luther J. Carter, Science, 200, 1135 (1978).
- 16. Peter Avotins, "Adsorption and Coprecipitation Studies of Mercury on Hydrous Iron Oxide," Ph.D. Dissertation, Stanford University, 1975.
- 17. K. C. Swallow and François Morel, "Adsorption of Trace Metals by Hydrous Ferric Oxide in Seawater," EPA-600/3-80-011, January, 1980.
- 18. D. G. Kinniburgh and M. L. Jackson, "Adsorption of Mercury(II) by Iron Hydrous Oxide Gel," Soil Sci. Soc. Am. J., 42, 45 (1978).
- 19. James R. Brown, G. Michael Bancroft, William S. Fyfe, and Ronald A. N. McLean, "Mercury Removal from Water by Iron Sulfide Minerals. An Electron Spectroscopy for Chemical Analysis (ESCA) Study," Envir. Sci. Tech., 13, 1143 (1979).
- 20. Prithviraj Mukherji and Dana R. Kester, "Mercury Distribution in the Gulf Stream," Science, 204, 64 (1979).
- 21. E. L. Schrader and William J. Furbish, "An Aqueous and Sedimentalogical Model for Heavy Metal Contamination of Stream Systems Affected by Sulfide Mining in the Eastern United States," Bull. Environm. Contam. Toxicol., 20, 159 (1978).
- 22. See for example, P. U. Sakellaridis and F. Z. Nobelis, J. Inorg. Nucl. Chem., 36, 2599 (1974).
- 23. E. Onat, J. Inorg. Nucl. Chem., 36, 2029 (1974).
- 24. K. Z. Doerffel, Z. Anal. Chem., 185, 91 (1962).
- 25. R. Puschel, Mikrochim. Acta, 783 (1968).

- 26. E. Lassner, Z. Anal. Chem., 222, 170 (1966).
- 27. E. Schwarz-Bergkampf, Z. Anal. Chem., <u>221</u>, 143 (1966).
- 28. Sabina Slavin, William B. Barnett and Herbert L. Kahn, Atomic Absorption Newsletter, 11, 37 (1972).

